Adiabatic and Non-Adiabatic Contributions to the Free Energy from the Electron-Phonon Interaction for Na, K, Al, and Pb

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The electron-phonon interaction is known to affect measurably a number of quantities. The low-temperature specific heat of metals for example is linear in temperature,

$$C = \left(\Gamma_{bs} + \Gamma_{ep} \right) T = \Gamma_{bs} \left(1 + \lambda \right) T$$

and consists of contributions from band structure (Γ_{bs}) and electron-phonon interaction (Γ_{ep}). λ depends on the material and is generally quite small for nearly free electron metals and of order 0.1. For transition metals or strongly correlated materials λ can be as large as 1.2–2 and become very important for our theoretical understanding of those materials. For instance, one can calculate the electronic

density of states at the chemical potential from the coefficient Γ_{bs} of the specific heat, which is an important quantity in theoretical models. Without accurate knowledge of the size of the effect of the electron-phonon interaction, λ, an accurate density of states cannot be extracted from experiment. A better understanding of the electron-phonon interaction is also important for other phenomena. The effect of superconductivity for example is caused by the effective interaction between electrons mediated by their interactions with phonons in a number of metals.

In this work we calculated the electron-phonon contribution to the free energy within the pseudopotential formalism up to second order in the interaction. The phonon spectrum was calculated from a Born-von Kármán force constant model and the pseudopotential from Harrison and Ashcroft pseudopotential models. We used appropriate parameters for four different metals, Na, K, Al, and Pb. We divided the free energy into an adiabatic and a non-adiabatic contribution. We calculated these separately for the four materials for temperatures between 0 and roughly 1.5 times the melting temperature. Previous authors have not calculated the electron-phonon contribution to the free energy in such detail. By looking at only
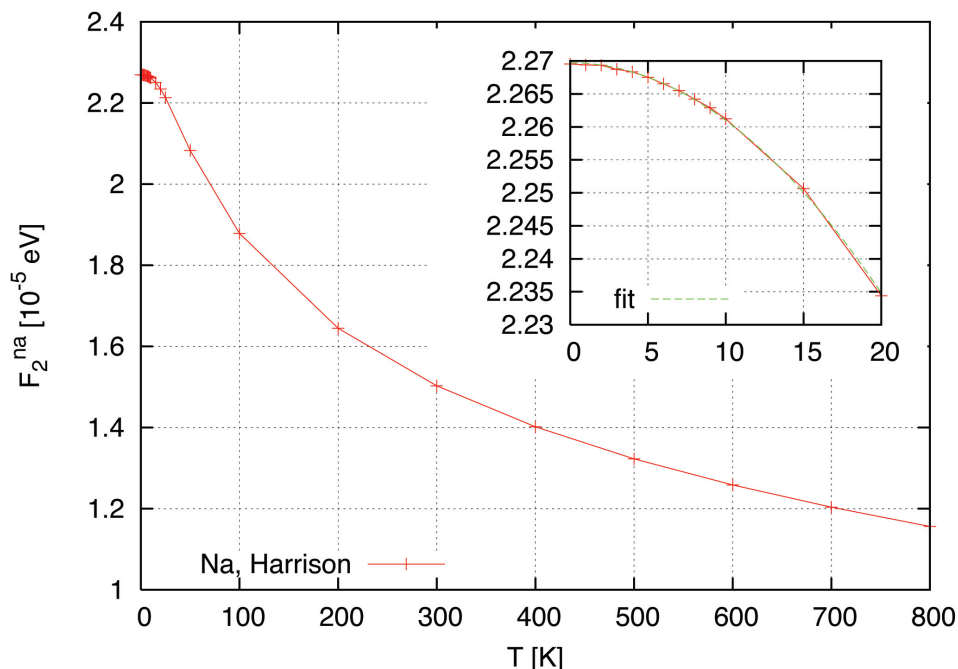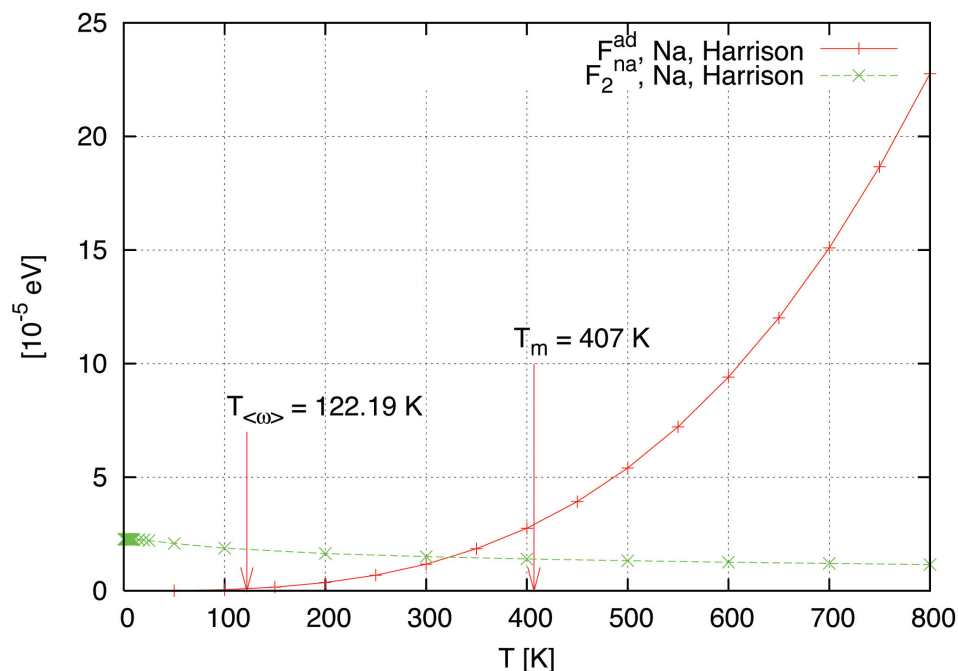
Figure 1—
The non-adiabatic contribution for Na using a Harrison pseudopotential model. Shown in the inset is a fit to the function $C_2 + A_2 T^2$.

limited ranges of temperature (Grimvall) or calculating the contribution to the entropy instead of the free energy (Allen), previous authors missed important details.

Figure 1 shows our result for the non-adiabatic contribution to the free energy for Na. From a Sommerfeld expansion at low temperatures we expect this contribution to go as $C_2 + A_2 T^2$ and the fit shown in the inset shows very good agreement with this form. We are able to extract the curvature A_2 and the zero temperature value C_2. C_2 has not been calculated previously because previous authors calculated only the entropy.

Figure 2 shows the adiabatic and the non-adiabatic contributions for Na. The adiabatic contribution exhibits quadratic temperature dependence at low temperatures and cubic dependence at high temperatures. Since the adiabatic approximation is equivalent to the classical limit for the ion motion, it should work well at high temperatures and it is therefore not surprising that it dominates the free energy at $T > 300K$. The non-adiabatic contribution, which can be understood as the quantum corrections to the classical behavior becomes more important for low temperatures and dominates in that regime. For reference we included the melting temperature of Na and the temperature of the average phonon frequency in the graph. The crossover between the adiabatic and the non-adiabatic contribution is at about 80% of the melting temperature and well above the average phonon frequency temperature.

Our results for K, Al, and Pb will be published elsewhere. Just as in Na we find that the crossover happens between the melting temperature and the temperature of the average phonon frequency.

From our results it is evident that care has to be taken when calculating the free energy or derived quantities. Because the crossover is at such high temperatures a typical phonon frequency in a metal cannot be used reliably to decide whether one is dealing with a high- or low-temperature regime. Our calculations suggest that for temperatures above the average phonon frequency to up to the melting temperature both the adiabatic and the non-adiabatic contributions to the free energy need to be evaluated, whereas at low temperatures the adiabatic contribution can be safely neglected.

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